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# The Kinetics of the Mercury(II)-Catalyzed Aquation of the Azidopentaaquochromium(III) Ion

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*The kinetics of the mercury(II)-catalyzed aquation of azidopentaaquochromium(III) ion has been studied over a range of* $Hg^{2+}$ *and* $H^+$ *concentrations at 60, 70.1 and 80° and ionic strength 1.0* M. *The aquation follows the rate equation* $-[d\ln(CrN_3^{2+})]/dt = \sum_i k_i(H^+)^i + \sum_j k_j^{Hg}(H^+)^j(Hg^{2+})$ *with* $i=1, 0, -1, -2$, *and with* $j=0, -1$, *and* $-2$. *The rate parameters at 25° and the activation parameters for the mercury(II)-catalyzed aquation have been computed.*

## Introduction

It has often been found that mercury(II) ion catalyzes aquatic dissociation of halide[2] and pseudohalide[2] ligands from transition metal complexes. A number of kinetic studies have been concerned with cobalt(III)[3] and chromium(III) complexes, and it is believed that the reaction of these substrates involves halide-bridged transition states. Certain complexes favour formation of binuclear intermediates with mercury(II) in amounts high enough to be observed or separated, such is the case with some complexes of *cis*-dihalido configuration[3,4,5,6] and with $Co(NH_3)_5CN^{2+}$,[7] $Cr(H_2O)_5NCS^{2+}$,[8,9] and $Cr(H_2O)_5CN^{2+}$,[10] complexes. For the comparison with the other monohalide-chromium(III) ions we studied the kinetics of the mercury(II)-catalyzed aquation of azidopentaaquochromium(III) as a

$$CrN_3^{2+} + Hg^{2+} \rightarrow Cr^{3+} + N_3^- + Hg^{2+} \qquad (1)$$

function of acidity and temperature.

## Experimental Section

*Materials.* All solutions were prepared with doubly distilled water. All chemicals used were analytical grade. Perchloric acid (Merck) and mercury(II) oxide (Kemika) were used without further purification. Magnesium perchlorate (Kemika) and sodium carbonate (Merck) were recrystallized three times from water. Sodium perchlorate solutions were prepared by neutralizing sodium carbonate with perchloric acid. Mercury(II) perchlorate solutions were prepared and analysed as previously described.[12] Azidochromium solutions were prepared by the both methods reported by King *et al.*[13,14] Molar absorbancy indices agreed very well with the published values.[14]

*Kinetics and Stoichiometry.* The kinetics of the reaction was followed spectrophotometrically at 280 nm where there is an adequate absorption difference between the reactants and the products. At 80° kinetics experiments were performed in the thermostated cell compartment of a Hilger H 700 spectrophotometer. At 60 and 70.1° aliquots of thermostated reaction mixtures were cooled and absorbances measured at room temperature. The reaction was initiated by an addition of thermostated azidochromium(III) solution to a thermostated solution containing all the other components. Mercury(II) perchlorate concentrations were at least twenty times in excess to those of azidochromium(III) ion, and the pseudo first order rate constants were calculated from the slopes of the straight lines obtained by plotting log $(D_t - D_\infty)$ *vs.* time, where $D_t$ and $D_\infty$ are the optical densities at time t and 8 to 10 half lives of the reaction, respectively. The initial concentrations of azidochromium(III) ion were in the range 1.5 to $4.3 \times 10^{-4}$ *M*. The ionic strength was maintained at 1.0 *M* with sodium perchlorate. Runs at 70.1° with $H^+ = 0.4$ *M* and at 60° with $H^+ = 0.1$ *M* were also performed at 1.0 *M* ionic strength maintained with magnesium perchlorate.

Stoichiometry of the reaction, assumed to be as given in equation 1, was checked by recording UV spectra of the reaction products and of the appropriate blank solutions by a Unicam S.P. 700 spectrophotometer. The blank solutions containing chromium(III) ion, azide ion, and other components in an equivalent amounts to those used in the kinetic runs showed identical spectra as the « infinite-time » samples. However, it vas observed that azide ion is involved in an equilibrium with mercury(II) ion giving species(es)

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[2] Hereafter halide.
[3] C. Bifano and R.G. Linck, *Inorg. Chem.*, *7*, 908 (1968) and the references therein.
[4] W.C. Waggener, J.A. Mattern, and G.H. Cartledge, *J. Amer. Chem. Soc.*, *81*, 2958 (1959).
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[7] H. Siebert, *Z. Anorg. Allgem. Chem.*, *327*, 63 (1964).
[8] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, *88*, 434 (1966).
[9] J.N. Armor and A. Haim, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept. 1968.
[10] J.P. Birk and J.H. Espenson, *Inorg. Chem.*, *7*, 991 (1968).
[12] M. Orhanović and N. Sutin, *J. Amer. Chem. Soc.*, *90*, 4286 (1968).
[13] D.L. Ball and E.L. King, *J. Amer. Chem. Soc.*, *80*, 1091 (1958).
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with an absorption maximum at 250 nm. Increasing mercury(II) ion concentration increases the absorbance at the maximum. The nature of the equilibrium was not examined.

A prolonged heating of the reaction products or of the blank solutions at the temperatures used for kinetics studies caused an increase in the UV absorption, probably due to the oxidation of azide ion by mercury(II) ion or by perchlorate ion. However, it did not interfere with the absorbance measurements at 8-10 half lives of the reaction.

## Results

The pseudo-first order rate constants observed for the mercury(II)-catalyzed aquation of azidochromium(III) ion at different hydrogen ion concentrations and different temperatures are shown in Figures 1 to 3. Suitable ranges of mercury(II) ion concentrations have been used to check for eventual departures from straightforward second-order kinetics. Two sets of runs ($H^+ = 0.4\ M$, $T = 70.1°$ and $H^+ = 0.1\ M$, $T = 60.0°$) have been performed having $1.0\ M$ ionic strength adjusted with magnesium perchlorate. The rate constants observed in sodium perchlorate media tend to have somewhat higher values than those in magnesium perchlorate, indicating that slight curvatures which appear in Figures 1 to 3 at plots with large ranges of mercury(II) ion concentrations, if significant at all, are due to the change of the medium, consisting primarily of 1:1 electrolyte at low and of 2:1 electrolyte at high mercury(II) ion concentrations.

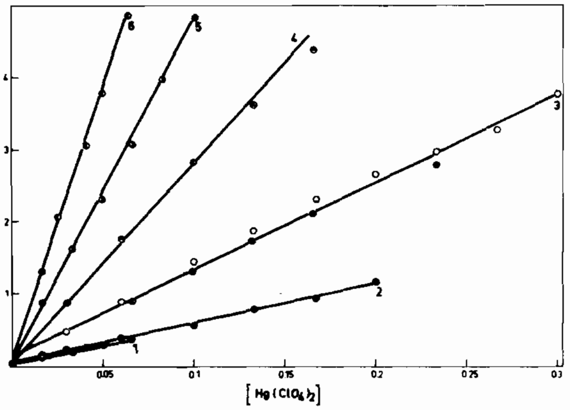

Figure 1. Plots of $k_{obs}$ *vs.* $(Hg^{2+})$ for the reaction of $Hg^{2+}$ with $CrN_3^{2+}$ at 60.0°, ionic strength 1.0 *M* ($NaClO_4$), and the following molar hydrogen ion concentrations: (1) 0.8, (2) 0.4, (3) 0.1,* = magnesium perchlorate media, (4) 0.0505, (5) 0.0301, (6) 0.0202.

The measured rate constants for the spontaneous aquation of azidochromium(III) ion, not all shown in the figures, are in an excellent agreement with those reported by Swaddle and King.[14] However, the intercepts of the straight lines in Figures 1 to 3 give higher values, most likely due to the medium effect. The computed slopes, *i.e.* the second-order rate constants for the mercury(II)-catalyzed aquation of azidochromium(III) ion at different hydrogen ion concentrations and temperatures are given in Table I. The uncertainties quoted are standard deviations.

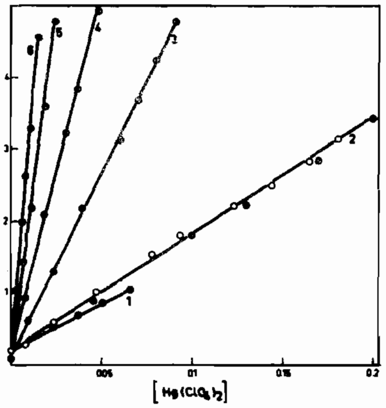

Figure 2. Plots of $k_{obs}$ *vs.* $(Hg^{2+})$ for the reaction of $Hg^{2+}$ with $CrN_3^{2+}$ at 70.1°, ionic strength 1.0 *M* ($NaClO_4$) and the following molar hydrogen ion concentrations: (1) 0.8, (2) 0.4,* = magnesium perchlorate media, (3) 0.1, (4) 0.0501, (5) 0.0296, (6) 0.0196.

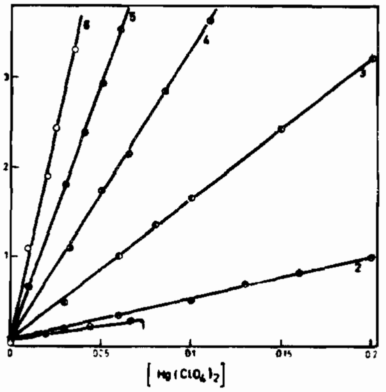

Figure 3. Plots of $k_{obs}$ *vs.* $(Hg^{2+})$ for the reaction of $Hg^{2+}$ with $CrN_3^{2+}$ at 80.0°, ionic strength 1.0 *M* ($NaClO_4$) and the following molar hydrogen ion concentrations: (1) 0.8, (2) 0.4, (3) 0.1, (4) 0.0504, (5) 0.031, (6) 0.021.

The data presented in Figures 1 to 3 and Table I are consistent with the generally expressed rate law

$$-[d\ln(CrN_3^{2+})]/dt = \sum_i k_i^s(H^+)^i + \sum_j k_j^{Hg}(H^+)^j(Hg^{2+}) \qquad (2)$$

The experimentally observed dependence of the first-order rate constant for the spontaneous aquation upon hydrogen ion concentration was resolved by Swaddle and King[14] into four terms, with *i* having values 1, 0, −1, and −2. The mercury(II)-catalyzed aquation of azidochromium(III) ion, corresponding to the second term in equation 2, involves three reaction paths in the acidity range studied. Using a CAE 90-40 computer, the second-order rate constants given in Table I were treated simultaneously for all temperatures according to the expression:

$$k^{Hg} = \left(\frac{kT}{h}\right)\sum_j (H^+)^j e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

**Table I.** Second-order rate constants for the mercury(II)-catalyzed aquation of azidochromium(III) ion at 1.0 *M* ionic strength ($NaClO_4$).

| $10^2H^+(M)$ | T(°) | $10^2k^{Hg}(M^{-1}sec^{-1})$ | $10^2H^+(M)$ | T(°) | $10^2k^{Hg}(M^{-1}sec^{-1})$ |
|---|---|---|---|---|---|
| 2.02 | 60.0 | 7.67±0.13 | 10.0 | 70.1 | 5.18±0.04 |
| 3.01 | 60.0 | 4.64±0.09 | 40.0 | 70.1 | 1.69±0.02 |
| 5.05 | 60.0 | 2.72±0.05 | 80.0 | 70.1 | 1.27±0.02 |
| 10.0 | 60.0 | 1.31±0.03 | 2.10 | 80.0 | 95.3 ±2.4 |
| 40.0 | 60.0 | 0.553±0.009 | 3.10 | 80.0 | 58.5 ±0.8 |
| 80.0 | 60.0 | 0.451±0.025 | 5.04 | 80.0 | 33.0 ±0.3 |
| 1.96 | 70.1 | 31.1 ±1.1 | 10.0 | 80.0 | 15.7 ±0.5 |
| 2.96 | 70.1 | 19.4 ±0.3 | 40.0 | 80.0 | 4.79±0.07 |
| 5.01 | 70.1 | 10.3 ±0.2 | 80.0 | 80.0 | 3.25±0.03 |

**Table II.** Rate and activation parameters for the reaction of $Hg^{2+}$ with $CrN_3^{2+}$.

| Quantity | $k_o$, $M^{-1}sec^{-1}$ | $k_{-1}$, $sec^{-1}$ | $k_{-2}$, $M\ sec^{-1}$ |
|---|---|---|---|
| $k_j^{Hg}$ at 25° | $1.1\times10^{-4}$ | $4.5\times10^{-6}$ | $4.9\times10^{-8}$ |
| $\Delta H^*$ kcal mole$^{-1}$ | 18.5±1.3 | 29.6±1.0 | 30.0±2.7 |
| $\Delta S^*$ cal mole$^{-1}$deg$^{-1}$ | —14.7±3.8 | 16.3±3.0 | 8.7±8.0 |

A nonlinear least-square program[15] was used to obtain the best values of the enthalpies and entropies of activation. Each rate constant was weighted according to the reciprocal of its square since the per cent error in $k^{Hg}$ was approximately constant. The best fitting was obtained with j having values 0, —1, and —2. The calculated values of the rate constants agreed with the values given in Table I with an average deviation of 2.5%. The activation parameters and the individual $k_j^{Hg}$ (equation 2) calculated by the program are summarized in Table II.[16]

## Discussion

The extreme lability of water coordinated to mercury(II) ion and relatively slow rates of the mercury(II)-catalyzed aquation of halide complexes of cobalt(III) and chromium(III) led to the suggestion that the latter reactions involve formation of the binuclear complex in a fast preequilibrium, followed by a rate-determining dissociation of the halide ligand. For monohalido complexes of chromium(III) previously studied the reacting scheme can be represented as

$$L_5CrX^{2+}+Hg^{2+}\rightleftarrows L_5CrXHg^{4+} \quad Q,\ \text{fast}$$

$$L_5CrXHg^{4+}\rightarrow L_5Cr(OH_2)^{3+}+HgX^+ \quad k^{Hg},\ \text{rate determining}^{17}$$

where $L=H_2O$, $NH_3$; $X=Cl$,[18,19] CN,[10] SCN,[12,20] NCS[8,9] giving for the rate constant observed

$$k_{obs}^{Hg}=\frac{kQ(Hg^{2+})}{1+Q(Hg^{2+})} \tag{3}$$

Expression 3 is reduced to $k^{Hg}_{obs}=kQ(Hg^{2+})$ for $CrCl^{2+}$, $Cr(NH_3)_5Cl^{2+}$, $Cr(SCN)^{2+}$, and now for $CrN_3^{2+}$, due to $1\gg Q(Hg^{2+})$, giving strict first-order kinetics in respect to mercury(II) ion concentration. The rate and activation parameters given in Table II thus represent associated kinetic and thermodinamic values. A high equilibrium constant (Q) for $CrNCS^{2+}$ reaction enabled Armor and Haim[9] to separate equilibrium and kinetic (k) contributions. A special situation arises with $CrCN^{2+}$,[10] where an excess of mercury(II) ion produces quantitatively $CrNCHg^{4+}$ ion, after the bond isomerisation has occurred.

It appears that soft mercury(II) ion has not affinity high enough for hard nitrogen sites of azide ligand in azidochromium(III) to make accumulation of the binuclear intermediate possible. However, a kinetically stable azide-bridged binuclear complex appears to be formed between $Hg^{2+}$ and *cis*—$Coen_2(N_3)_2^+$,[5] probably due to favorable *cis*-configuration and to the lower charge of the complex.

A speculation could be put forward concerning acidity dependence of the reaction 1. As pointed out by Espenson *et al.* for monochlorochromium(III) complexes,[18,19] and later found for the other chromium(III) complexes which follow first-order kinetics in respect to mercury(II) ion concentrations[6,12,21] the catalyzed aquation shows the same acidity dependence as the corresponding spontaneous aquation, suggesting may be that the reaction proceeds between $Hg^{2+}$ ion and the complex specieses present in the hydrolitic equilibria. The absence of the $(H^+)^1$ term for the catalyzed aquation of $CrN_3^{2+}$ (equation 2), which is observed for the spontaneous aquation may be due to the proton situated at the azido ligand and to the higher charge of the relevant species. However, if $Hg^{2+}$ even

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(15) We are grateful to Dr. N. Sutin for supplying this program and to Dr. L. Klasinc for adapting it for CAE 90-40 computer.

(16) A more exact treatment of $k_j^{Hg}$ upon ($H^+$) dependence would require a correction to be made due to the hydrolytic equilibria of mercury(II), particularly at low ($H^+$) used. The lack of literature data on the values of equilibria constants for the medium and temperatures used in this work made us to neglect the correction. The linearity of the plots in Figures 1-3 gives a support to such a simplified approach since a substantial degree of hydrolysis would have caused a trend of departure from linearity with the increase of mercury(II) concentration.

(17) The dissociation of the binuclear complex appears to be a two-step process. F.F. Ferraris and E.L. King (*J. Amer. Chem. Soc.*, 92, 1215 (1970)) have made an observation consistent with the formation of a common intermediate, presumably pentaaquochromium(III) ion, in mercury(II)-catalyzed solvolysis reactions of halochromium(III) ions.

(18) J.H. Espenson and J.P. Birk, *Inorg. Chem.*, *4*, 527 (1965).

(19) J.H. Espenson and S.R. Hubbard, *Ibid.*, *5*, 686 (1966).

(20) M. Orhanović and N. Sutin, *J. Amer. Chem. Soc.*, *90*, 538 (1968).

(21) This work.

is the only reacting mercury(II) species still different reaction mechanisms can be operating for the pathways represented with $j=-1$ and $-2$ since hydrolytic equilibria of the binuclear intermediate may also be involved.[22]

It is interesting to note that in chromium(II)-catalyzed aquation of $CrN_3^{2+}$, where an inner-sphere redox mechanism involving hydroxy-bridged transition state was proposed,[23] only $(H^+)^0$ and $(H^+)^{-1}$ terms in the rate law have been observed. A range of high acidities was used, however.

*Acknowledgments.* We wish to thank Miss. V. Butković and Miss Z. Božičević for the help with some experiments.

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[23] J. Doyle, A.G. Sykes, and A. Adin, *J. Chem. Soc. (A)*, *1968*, 1314.